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Catalase activity of coarse-grained and nanosized oxide tungsten bronzes obtained by electrolysis of molten salts*

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Nanocrystalline samples of $K_xLi_yWO_3$ with hexagonal structure obtained by electrodeposition of molten salts were several times more active in catalytic decomposition than the coarse-grained materials.

Key words: oxide tungsten bronzes, nanocrystals, electrolysis of molten salts, catalase activity.

Manufacture of highly active and selective catalysts is a priority direction of development of catalytic technologies. Size of crystallites exerts a considerable effect on the catalytic properties of crystalline systems. Presently, dispersed and bulk materials containing structural units (grains, crystallites, blocks, and clusters), whose geometric sizes do not exceed 100 nm in at least one direction are conventionally attributed to nanomaterials. These materials have qualitatively new properties and functional and operating characteristics.[1] The control of the composition and structural and size characteristics of nanocrystalline systems, including oxide systems, enables a targeted design of highly active catalysts.

Oxide tungsten compounds, including bronzes, are used as catalysts in industrially important processes of organic synthesis and petrochemistry.[2] They prove themselves to be good catalysts in the production of epoxide, hydroxyaromatic, and carbonyl compounds, quinones, cellulose (oxidative delignification of wood), and other products.[3,4] Oxide tungsten compounds exhibit catalytic activity in deep desulfurization of petroleum products.[5,6] Improvement of this process is an urgent task, because maximum allowable concentrations (MAC) for sulfur in gasolines and diesel oil become increasingly tougher and with conventional industrial hydrodesulfurization it is not possible to attain the depth of desulfurization corresponding to the MAC indicated in the recent ecological standards EURO-5 and EURO-4 (10—40 ppm).

The purpose of the present work is to establish a relationship between the structure and dispersion of samples of oxide tungsten bronzes (OTB), including nanocrystalline OTB, obtained by electrolysis of molten salts, and their catalytic activity in the model reaction of hydrogen peroxide decomposition (catalase activity). This test is convenient for screening studies of potentially efficient catalytic systems of peroxide oxidation of organic substrates[7]

$$2\,H_2O_2 \xrightarrow{i} O_2 + 2\,H_2O$$

i. OTB.

Experimental

Nanocrystalline samples of OTB were obtained by the electrolysis of the melt $K_2WO_4 : Li_2WO_4 : WO_3 = 0.30 : 0.25 : 0.45$. A platinum wire was used as an anode, a tungsten foil served as a cathode, and a platinum—oxygen reference electrode was used. An overvoltage pulse (η) of 170—300 mV with a certain duration (τ) was fed to the cell. This resulted in the formation of a crystalline precipitate on the tungsten cathode. The precipitate was swept from the support, thoroughly scoured, and dried. The samples obtained were examined by X-ray diffraction analysis, and dispersion was analyzed on a RIGAKU DNAX 2200PC apparatus. The morphology of the precipitates was determined using a JSM-5900 LV electron microscope. The specific surface area was measured using the BET method on a SORBI 4.1 instrument.

We found that the obtained nanocrystalline material was a powder of hexagonal bronze consisting of microcrystals, where each microcrystal is an oriented nanosized needle structure. All needles have one orientation and extended towards the direction [0001]. The thickness of the needles is about 30—100 nm.

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The bronze powder obtained by the trituration of large (more than 0.5 mm) single crystals of the precipitate has different morphology.

Coarse-grained bronzes $K_xLi_yWO_3$ (y = 0.05) of hexagonal structure were also prepared by the electrolysis of the melt $K_2WO_4 : Li_2WO_4 : WO_3 = 0.30 : 0.25 : 0.45$ at 700 °C, and tetragonal bronzes were prepared according to manual data.[8] The more detailed procedure for the preparation of these bronzes and the modes of preparation of cubic sodium—tungsten bronzes have been published earlier.[9]

Comparative kinetic studies of the decomposition of hydrogen peroxide in the presence of bronze samples were carried out in a temperature-controlled reactor equipped with a reflux condenser, where an aqueous solution of H_2O_2 was stirred using air bubbling. The reaction temperature was 50 °C. The initial concentration of H_2O_2 was 0.64 mol L^{-1}, and a weighed sample was 0.1 g. In order to minimize errors in the work with the nanosized catalysts, the process was stopped after some time, and the solution was decanted and centrifuged at 6000 rpm. The content of remained hydrogen peroxide was determined by the iodometric method according to a described procedure.[10] The duration of each process was 5, 10, 20, and 30 min.

The obtained functions of concentrations were approximated by polynomials. The initial reaction rates were determined by graphical differential and interpolation. The error of determination was at most ±10%.

Results and Discussion

The study is based on the new method for synthesis of nanocrystalline OTB by electrolysis of the corresponding salts developed at the Institute of High-Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences.[11] Currently we were able to synthesize nanocrystalline hexagonal $K_xLi_yWO_3$. The method is characterized by good reproducibility of results and makes it possible to obtain high-purity bronzes, including nanocrystalline precipitates resistant to agglomeration of particles.

The synthesis gave a powder consisting of microparticles, whose structure contains oriented nanosized needles. All needles have one orientation and are extended towards the direction [0001]. The specific surface area of the nanocrystalline powders obtained at an overvoltage of 200 mV is 0.92 m^2 g^{-1}. Figures 1—3 show nanocrystals of the OTB precipitate. The X-ray method of determination of dispersion of the samples showed that in the precipitate of nanocrystalline bronze presented in Figs 2 and 3 the average size of the needles is 32.1±0.3 nm. This morphology of the precipitate is directly related to the mechanism of formation of hexagonal oxide tungsten bronze during electrolysis of the melt.

So far, the conditions of preparation were determined only for hexagonal nanocrystalline OTB $K_xLi_yWO_3$, although the pulse electrochemical method of preparation of OTB precipitates makes it possible to synthesize nanosized crystals with different structures.

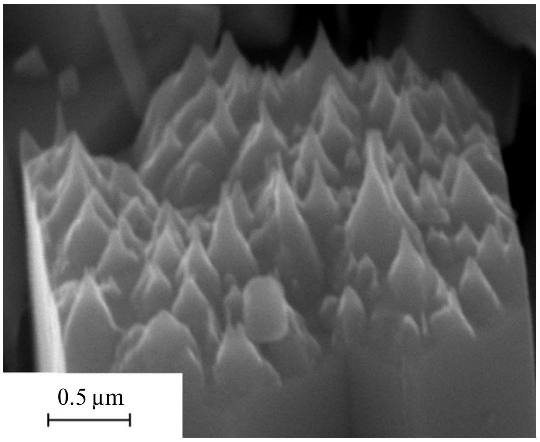

Fig. 1. Morphology of the $K_xLi_yWO_3$ precipitate microcrystal obtained by the electrolysis of molten salts in a pulse potentiostatic mode: T = 750 °C, η = 300 mV, and τ = 0.1 s.

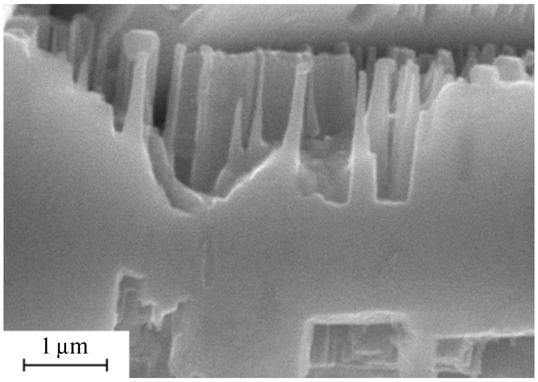

Fig. 2. Morphology of the $K_xLi_yWO_3$ precipitate microcrystal obtained by the electrolysis of molten salts in a pulse potentiostatic mode: T = 700 °C, η = 200 mV, and τ = 0.5 s.

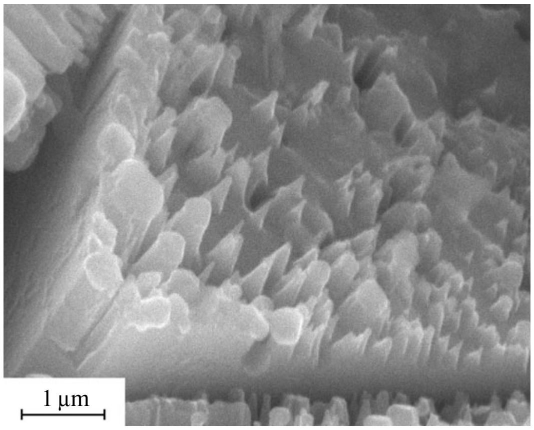

Fig. 3. Morphology of the coating surface on the tungsten plate. The precipitate of $K_xLi_yWO_3$ was obtained by the electrolysis of molten salts in a pulse potentiostatic mode: T = 700 °C, η = 200 mV, and τ = 0.5 s.

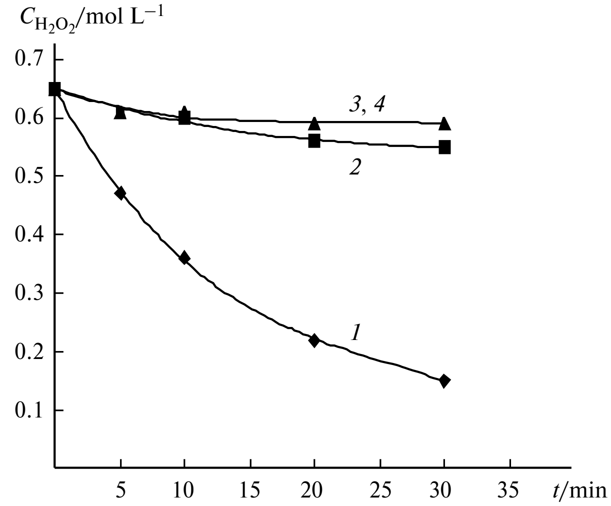

Fig. 4. Kinetic curves of H_2O_2 decomposition in the presence of the OTB samples: *1*, $K_xLi_yWO_3$ (hexagonal structure, nanocrystalline powder); *2*, $Na_{0.88}WO_3$ (cubic structure); *3*, $K_{0.475}WO_3$ (tetragonal structure); and *4*, $K_xLi_yWO_3$ (hexagonal structure).

To obtain comparative data on the catalase activity of the nanosized and coarse-grained samples of OTB, we studied the samples of hexagonal $K_xLi_yWO_3$ and also cubic $Na_{0.88}WO_3$ and tetragonal $K_{0.475}WO_3$. The specific surface area of these coarse-grained samples ranges from 0.2 to 0.4 m^2 g^{-1}. Since the sample of coarse-grained hexagonal OTB exhibited a low catalase activity, it was additionally triturated in a porcelain mortar until the particles with a specific surface area of 7.0 m^2 g^{-1} were obtained. In this case, particular particles are not regular and their size exceed 100 nm.

Figure 4 presents the kinetic curves of hydrogen peroxide decomposition in the presence of nanosized and coarse-grained powders of oxide tungsten bronze. It is shown that the catalytic activity of the powder of hexagonal tungsten bronze obtained by trituration of single crystals is low in spite of its high specific surface area.

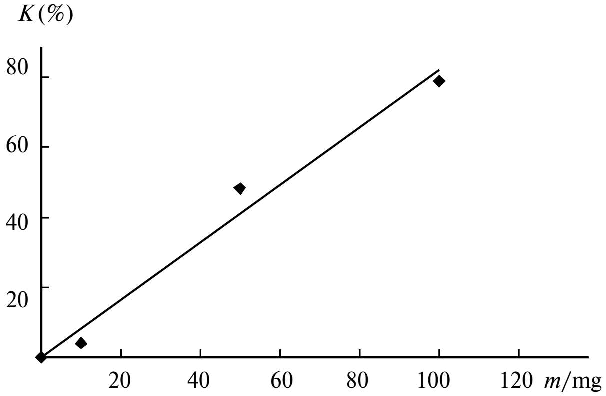

Fig. 5. Conversion of hydrogen peroxide (K) *vs* weight of the nanocrystalline catalyst $K_xLi_yWO_3$ (C_0 = 0.64 mol L^{-1}, 50 °C, 30 min).

The initial rates of decomposition (W_0) and the specific conversions (K_{sp}) of hydrogen peroxide within 30 min in the presence of OTB of various structures are listed in Table 1. It is seen that the activity of nanocrystalline hexagonal OTB $K_xLi_yWO_3$ exceeds the activity of the coarse-grained samples by an order of magnitude. The decomposition of H_2O_2 without a catalyst within 30 min is insubstantial under the above presented conditions, because the conversion of hydrogen peroxide is within the experimental error and does not exceed 2—3%. The dependence of the conversion of H_2O_2 on the amount of nanocrystalline OTB is presented in Fig. 5 and seems to be linear.

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Table 1. Catalytic activity of the oxide tungsten bronzes in H_2O_2 decomposition

Sample	Composition (isostructural compound)	S_{sp} /m^2 g^{-1}	K_{sp} /mmol g^{-1}	W_0 /mol L^{-1} h^{-1}
Powder of cubic structure	$Na_{0.88}WO_3$	0.390	9.5	0.39
Powder of tetragonal structure	$K_{0.475}WO_3$	0.225	4.5	0.31
Powder of hexagonal structure obtained by trituration of single crystals	$K_xLi_yWO_3$ ($K_{0.26}WO_3$)	7.000	0.2	0.29
Nanocrystalline powder of hexagonal structure	$K_xLi_yWO_3$ ($K_{0.26}WO_3$)	0.920	47.8	3.00

Note. S_{sp} is the specific surface of the OTB sample, K_{sp} is the specific conversion of H_2O_2 within 30 min, and W_0 is the initial rate of H_2O_2 decomposition.

References

1. A. G. Kolmakov, M. I. Alymov, *Perspektivnye materialy* [*Perspective Materials*], 2006, No. 5, 5 (in Russian).
2. M. T. Mirza, J. R. Walls, S. A. A. Jayaweera, *Thermochim. Acta*, 1989, **152**, 203.
3. S. Yu. Menrshikov, A. V. Vurasko, L. A. Petrov, V. L. Volkov, *Neftekhimiya*, 1992, **32**, 162 [*Petroleum Chemistry* (*Engl. Transl.*), 1992, **32**].
4. L. G. Maksimova, T. A. Denisova, L. V. Kristallov, V. G. Kharchuk, N. A. Zhuravlev, V. L. Volkov, L. A. Petrov, *Zh. Neorg. Khim.*, 1995, **40**, 976 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1995, **40**].
5. A. V. Anisimov, A. V. Tarakanova, *Ros. Khim. Zh.*, 2008, **52**, No. 4, 31 [*Mendellev Chem. J.* (*Engl. Transl.*), 2008, **52**, No. 4].
6. A. Chica, A. Corma, M. E. Dómine, *J. Catal.*, 2006, **242**, 299.
7. V. R. Pen, N. V. Karetnikova, I. L. Shapiro, I. V. Miroshnichenko, *Uspekhi sovremennogo estestvoznaniya* [*Progress in Modern Natural Science*], 2010, No. 9, 212 (in Russian).
8. K. P. Tarasova, V. A. Nazarov, N. O. Esina, *Trudy in-ta elektrokhimii UNTs AN SSSR* [*Works of the Institute of Electrochemistry Acad. Sci. USSR*], 1974, No. 21, 61 (in Russian).
9. A. N. Baraboshkin, K. P. Tarasova, V. A. Nazarov, Z. S. Martemryanova, *Trudy in-ta elektrokhimii UNTs AN SSSR* [*Works of the Institute of Electrochemistry Acad. Sci. USSR*], 1973, No. 19, 44 (in Russian).
10. *Spravochnik khimika* [*Chemistrs Manual*], Goskhimizdat, Moscow, 1962 (in Russian).
11. Pat. RF 2354753, *Byull. Izobr.* [*Inventionrs Bulletin*], 2009, No. 13 (in Russian).

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